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SULFATE CONTROL TECHNOLOGY ASSESSMENT, PHASE I: LITERATURE SEARCH AND ANALYSIS

William R. Leppard

Exxon Research and Engineering Company

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16. ABSTRACT

The report covered the following four areas: 1. Thermo-dynamics of Sulfuric Acid Production. At typical catalyst temperatures, conversions of SO_2 to SO_3 greater than 50% are thermodynamically possible. Equilibrium conversion is strongly dependent upon oxygen concentration. Exhaust SO_3 may hydrate to gaseous sulfuric acid within the vehicle's exhaust system, and the gaseous sulfuric acid will begin to condense at about 150°C. 2. Reaction of Sulfur Dioxide and Trioxide with Exhaust Gas Constituents and Exhaust System Components. Results show that the formation of ammonium sulfate is favorable only below 225°C, the reduction of both sulfur oxides by CO is favorable, reaction of both oxides with the iron oxide surface of exhaust system is favorable below 425°C and the reaction of SO_3 with the aluminum oxide catalyst substrate is possible below 425°C. 3. Automotive Catalysis of Sulfur Dioxide. The rate limiting step in the catalytic oxidation of SO_2 is the surface reaction between adsorbed oxygen and adsorbed SO_2. Literature search indicates that automotive catalysis literature is limited and inconclusive. 4. Sulfate Traps. The most promising means of removing SO_3 from the exhaust stream is to react it with a basic metal oxide. Based on a requirement selection criterion, the most promising sorbent material is C_aO. Other less promising but still attractive sorbents are the oxides of magnesium, M_n, and A_l.

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by

William R. Leppard

Exxon Research and Engineering Company
Products Research Division
Linden, New Jersey 07036

Contract No. 68-03-0497

EPA Project Officer: Joseph H. Somers

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Introduction

This literature search was conducted to bring together and examine the literature pertaining to the fate of sulfur oxides in automotive exhaust systems. Currently available gasoline averages about 300 ppm sulfur in the form of organic sulfur compounds. During the combustion process gasoline sulfur is oxidized to sulfur dioxide. In non-catalyst vehicles, this sulfur dioxide is emitted to the atmosphere. In vehicles equipped with oxidation catalysts for control of carbon monoxide and hydrocarbon emissions, further oxidation to sulfur trioxide takes place. This can then combine with water, forming sulfuric acid. The literature was reviewed to investigate the thermodynamic potential and kinetics of forming the trioxide and to examine the fate of both oxides in the exhaust system. Since sulfuric acid emissions may be deleterious, the literature pertaining to removal of sulfur oxides from gaseous streams was reviewed. Stress was placed on the use of metal-oxide sorbents for this purpose.

To cover these subjects, the body of this report is divided into four sections. The first section details the thermodyanmics of sulfur trioxide formation, reaction with water, and condensation. The second section examines possible reaction with materials in the exhaust gas or system. The third system reviews the catalytic oxidation of sulfur dioxide on platinum catalysts. The last section examines possible means of removing sulfur trioxide from the exhaust stream.

Summary and Conclusions

Thermodynamics of Sulfuric Acid Production

1. At typical oxidation catalyst temperatures, conversions of sulfur dioxide to sulfur trioxide greater than 50% are thermodynamically possible.

2. The equilibrium conversion is strongly dependent upon oxygen concentration. At temperatures above 400°C, decreasing the oxygen concentration decreases the equilibrium conversion, suggesting a possible control strategy.

3. Thermodynamics and kinetics show that exhaust sulfur trioxide may hydrate to gaseous sulfuric acid within the vehicles exhaust system, depending upon driving mode.

4. Thermodynamics show that the gaseous sulfuric acid will begin to condense at about 150°C which is below the temperature at the tailpipe exit for all driving modes except startup.

Reaction of Sulfur Dioxide and Trioxide with Exhaust Gas Constituents and Exhaust System Components

1. Thermodynamics shows that ammonia will reduce sulfur trioxide to the dioxide. However, exhaust ammonia will be oxidized over the oxidation catalyst before reaction can take place.

2. The formation of ammonium sulfate is favorable only below 225°C.

3. Thermodynamics shows that the reduction of both sulfur oxides by carbon monoxide is favorable.

4. Reaction of both oxides with the iron oxide surfaces of the exhaust system is favorable below 425°C.

5. Reaction of sulfur trioxide with the aluminum oxide catalyst substrate is possible below 425°C. The presence of carbon monoxide may lower this temperature by about 50°C.

Automotive Catalysis of Sulfur Dioxide

1. The rate limiting step in the catalytic oxidation of sulfur dioxide is the surface reaction between adsorbed oxygen and adsorbed sulfur dioxide.

2. The following rate equation appears to represent best the available experimental data for industrial catalysis and should be valid for automotive catalysis

$$\text{rate} = \frac{k_1 \left(P_{SO_2} P_{O_2}^{1/2} - \frac{P_{SO_3}}{K^e}\right)}{\left(1 + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{SO_3} P_{SO_3}\right)^2}$$

where k_1 is the rate constant, subscripted P's are the partial pressures of the compounds in the subscripts, K^e is the equilibrium constant of the oxidation reaction, and the subscripted K's are the absorption equilibrium constants for the compounds in the subscripts.

This equation is in accord with the above rate limiting mechanism. This equation also indicates a possible control strategy of limiting the amount of oxygen over the catalyst.

3. The automotive catalysis literature is limited. In addition the data are confounded by many experimental problems, notably the storage/release phenomenon. In general, this literature says that more sulfur trioxide is formed over catalysts than with non-catalyst vehicles but good quantitative data are lacking.

Sulfate Traps

1. The most promising means of removing sulfur trioxide from the exhaust stream is to react it with a basic metal oxide.

2. Based on a selection criterion consisting of seven requirements, the most promising sorbent material is calcium oxide. Other less promising but still attractive sorbents are the oxides of magnesium, manganese, and aluminum.

I. Thermodynamics of Automotive Sulfuric Acid Production

In assessing the production and fate of sulfuric acid within a vehicles engine or exhaust system, there are three basic reactions which must be considered. These reactions are: the reaction of sulfur dioxide with oxygen to form sulfur trioxide, the hydration of the sulfur trioxide to gaseous sulfuric acid, and the condensation of the gaseous acid to produce a finely dispersed aerosol. The first reaction is important as it shows that the formation of substantial amounts of sulfur trioxide is thermodynamically possible at typical automotive catalyst temperatures. The second and third reactions are important since they define the state, sulfur trioxide, gaseous sulfuric acid, or condensed sulfuric acid aerosol, in which the sulfur trioxide will exist in the exhaust system. This is important from the point of view of controlling the potential emissions within the exhaust system. Hydration of the trioxide is possible during some driving modes. Condensation, however, is unfavorable except possibly at start-up and idle.

A. Thermodynamics of Sulfur Trioxide Production

The reaction of sulfur dioxide with oxygen can proceed either homogeneously or catalytically. The homogeneous reaction is extremely slow [14] and would be negligible considering the very small residence times within the vehicle, typically on the order of a few seconds. In the presence of oxides of nitrogen, the rate of sulfur dioxide oxidation is increased markedly. A calculation using the rate-constant data from Duecker and West [14] shows that under high NO conditions, such as high speed or load, the conversion of sulfur dioxide to the trioxide would be ~1.0%. Since the reaction rate depends on the square of the NO partial pressure, the conversion would be much less under low NO conditions. The heterogeneous catalysis of this reaction will be discussed later.

No matter how rapid the reaction rate, the maximum conversion will be limited by thermodynamic equilibrium. Table 1 [48] lists the free energies and equilibrium constants for the reaction as written

$$SO_2(g) + 1/2\ O_2(g) \rightleftharpoons SO_3(g). \qquad (1)$$

The equilibrium constant for this reaction is

$$Ke = \frac{\left(P_{SO_3}\right)}{\left(P_{O_2}\right)^{1/2}\left(P_{SO_2}\right)} \qquad (2)$$

where P indicates component partial pressure in atmospheres. Figure 1 shows the effect of temperature on the conversion for typical exhaust gas compositions. Lines of different oxygen concentration are shown to illustrate the effect of differing air injection rates upstream of an automotive oxidation catalyst. As this figure illustrates, increasing the oxygen content of the exhaust increases the maximum possible conversion to sulfur trioxide. In the region of typical oxidation catalyst temperatures, 500 to 650°C, the maximum possible conversion is between 90 and 50% when using an air pump supplying 5% oxygen. Assuming that equilibrium controls the oxidation of sulfur dioxide, operation of the vehicle at stoichiometric or slightly lean air-to-fuel ratios, either by careful carburetion or by using a three-way catalyst system, the production of sulfur trioxide could be

TABLE 1

Equilibrium Constants for the Oxidation of Sulfur Dioxide to Sulfur Trioxide

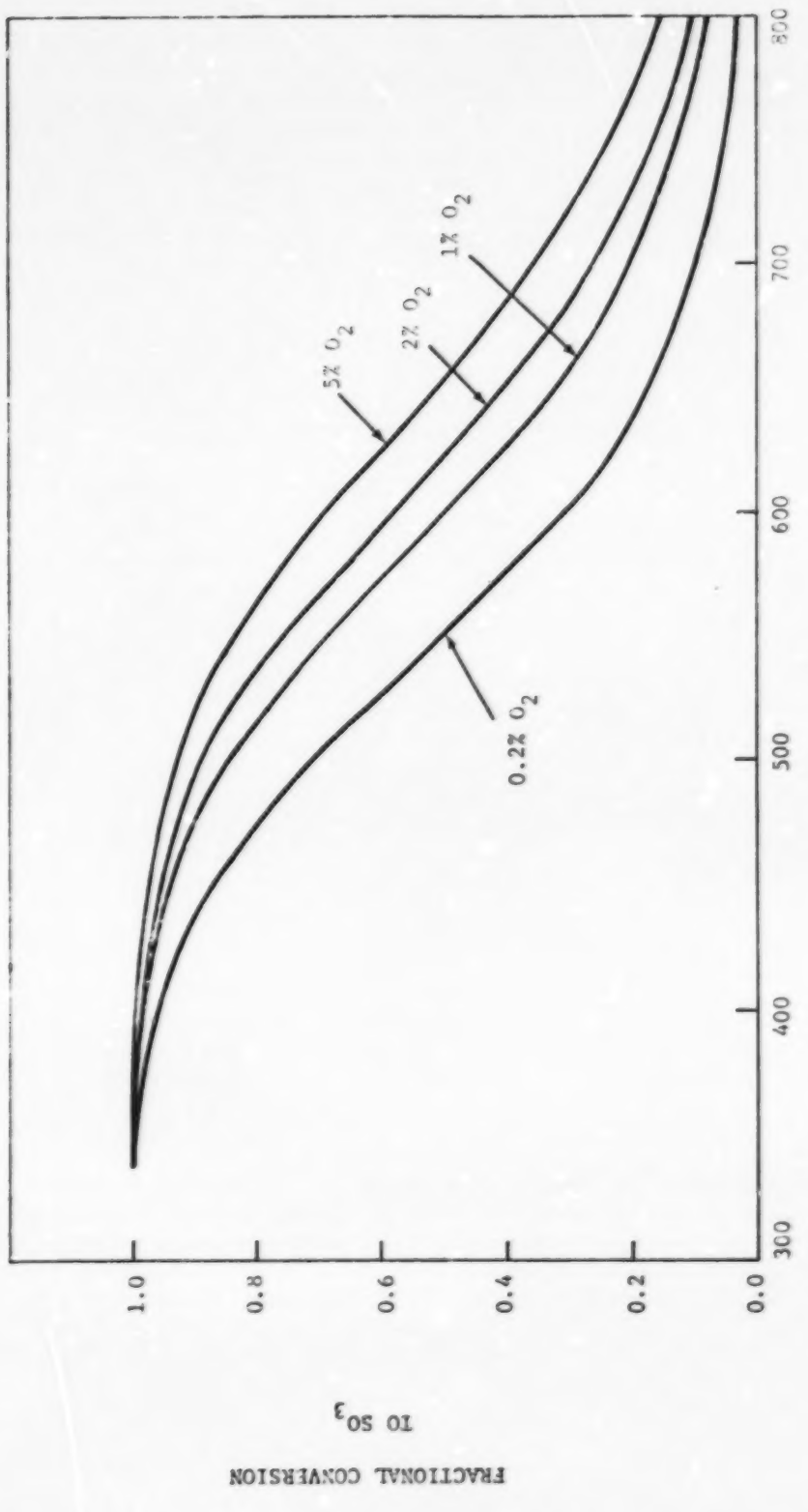
Temperature (°K)	Free Energy of Reaction (K cal/mole)	Equilibrium Constant (atm $^{-1/2}$)
300	-16906.50	2.069×10^{12}
350	-15775.99	7.088×10^{9}
400	-14649.01	1.008×10^{8}
450	-13520.27	3.682×10^{6}
500	-12389.19	2.600×10^{5}
550	-11257.38	2.972×10^{4}
600	-10127.01	4.892×10^{3}
650	- 8999.82	1.061×10^{3}
700	- 7876.73	2.878×10^{2}
750	- 6757.71	9.313×10^{1}
800	- 5642.04	3.477×10^{1}
850	- 4528.59	1.460×10^{1}
900	- 3416.23	6.754
950	- 2304.12	3.389
1000	- 1192.02	1.392
1050	- 80.38	1.039
1100	+ 1029.68	6.244×10^{-1}

reduced. For instance, operation at 0.2% oxygen instead of 5% could reduce the conversion by 25 to 65% over the typical oxidation-catalyst temperature range. However, at the lower temperatures absolute conversions could still be as high as 70% at the 0.2% level. Therefore, from an equilibrium standpoint, reduction of the oxygen content of the exhaust could result in lowering sulfur trioxide production, however, absolute control would not be feasible. The kinetics of this reaction will be discussed in the Automotive Catalysis section.

Figure 1

Equilibrium Conversion

$SO_2(g)+1/2\ O_2(g) \rightleftharpoons SO_3(g)$



B. Thermodynamics of Sulfur Trioxide Hydration

As the SO_3 produced by the engine or over an oxidation catalyst proceeds through the exhaust system, it is cooled significantly. As the temperature drops, the hydration of sulfur trioxide to gaseous sulfuric acid becomes more favorable as shown in Figure 2, where the fraction of sulfure trioxide hydrated to gaseous sulfuric acid is given as a function of temperature. This plot was generated using equilibrium constants calculated from Eqn. (17) of Gmetro and Vermeulen [20]. Hydration begins at about 450°C and is complete at about 200°C. Typical tailpipe exit temperatures range from ~200 to over 500°C [our measurements, 24] for conditions from idle to extended high speed driving. Thus, it is possible for sulfur trioxide to either survive throughout the exhaust system or to be completely hydrated de ending upon the driving mode. Gillespie and Johnstone [19] in studying sulfuric acid formation found that dry sulfur trioxide would form an aerosol instantaneously upon contact with moist air. These results imply that the hydration reaction is extremely rapid and would be controlled by equilibrium in an exhaust gas environment.

C. Thermodynamics of Sulfuric Acid Condensation

The dew point of gaseous sulfuric was experimentally determined and compared with calculated thermodynamic values by Lisle and Sensenbaugh [39]. They found excellent agreement. The calculated dew point as a function of temperature is shown in Figure 3. More recently, Verhoff and Banchero [56] have reviewed the literature concerning sulfuric acid dew points and correlated the data which they felt were accurate. The resulting least squares correlation is shown in Figure 3 for a water content of 12%. As this figure shows, both curves predict dew points within a few degrees of each other in the range applicable to exhaust sulfuric acid levels.

A vehicle operating at an air-to-fuel ratio of 15:1 using an average fuel of 300 ppm sulfur would produce exhaust containing approximately 10 ppm H_2SO_4 assuming 50% conversion of sulfur dioxide to trioxide. At this concentration, condensation would begin at ~133°C which is below the exhaust temperature at the tailpipe exit. The rate of condensation, as pointed out previously, is very rapid, therefore, should the exhaust temperature drop below 133°C, condensation of the gaseous sulfuric acid would immediately occur in the tailpipe. However, for the majority of driving situations, the sulfuric acid would exit the tailpipe in the vapor rather than the condensed state.

Figure 2

Equilibrium Conversion

$SO_3(g) + H_2O(g) == H_2SO_4(g)$

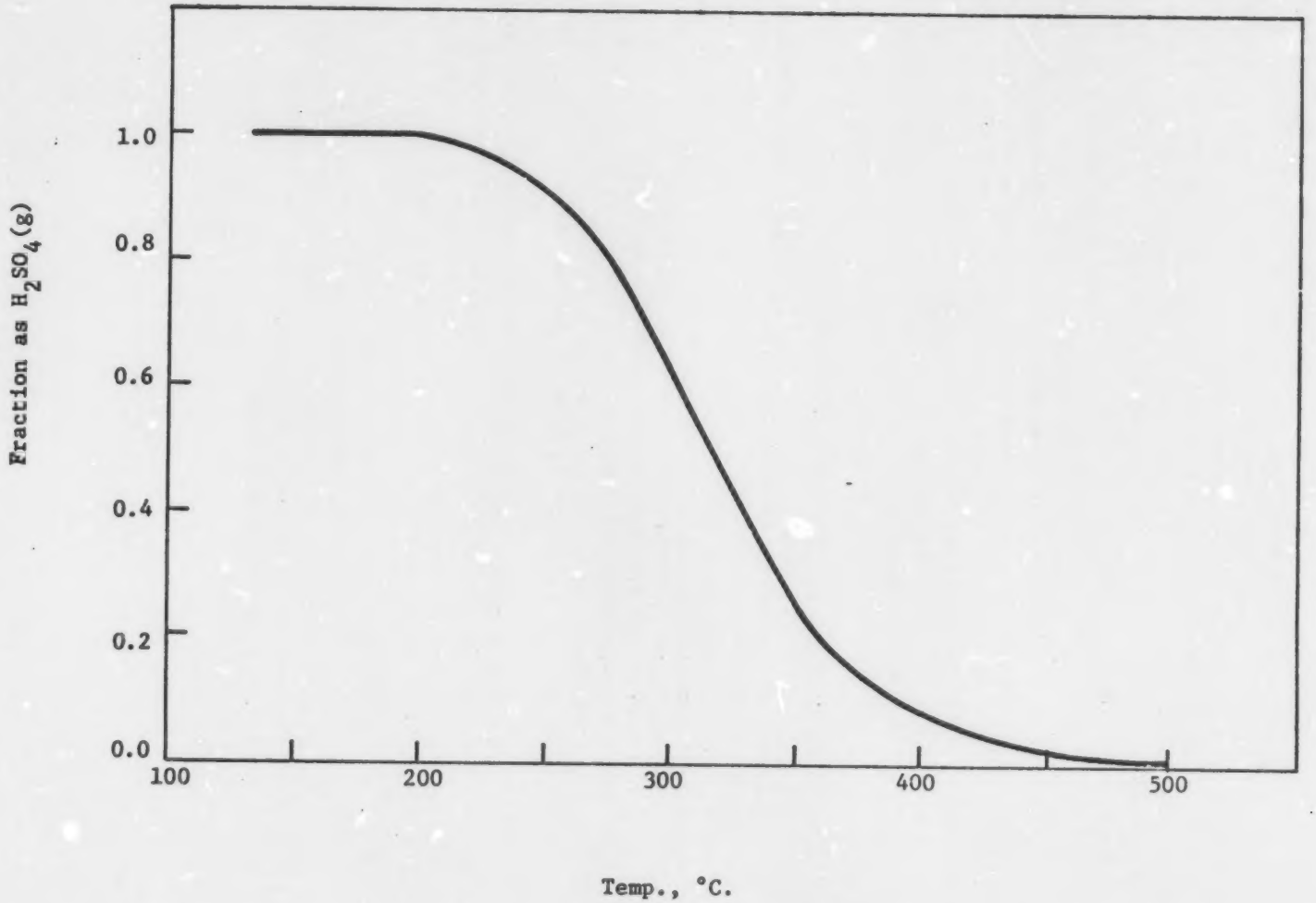
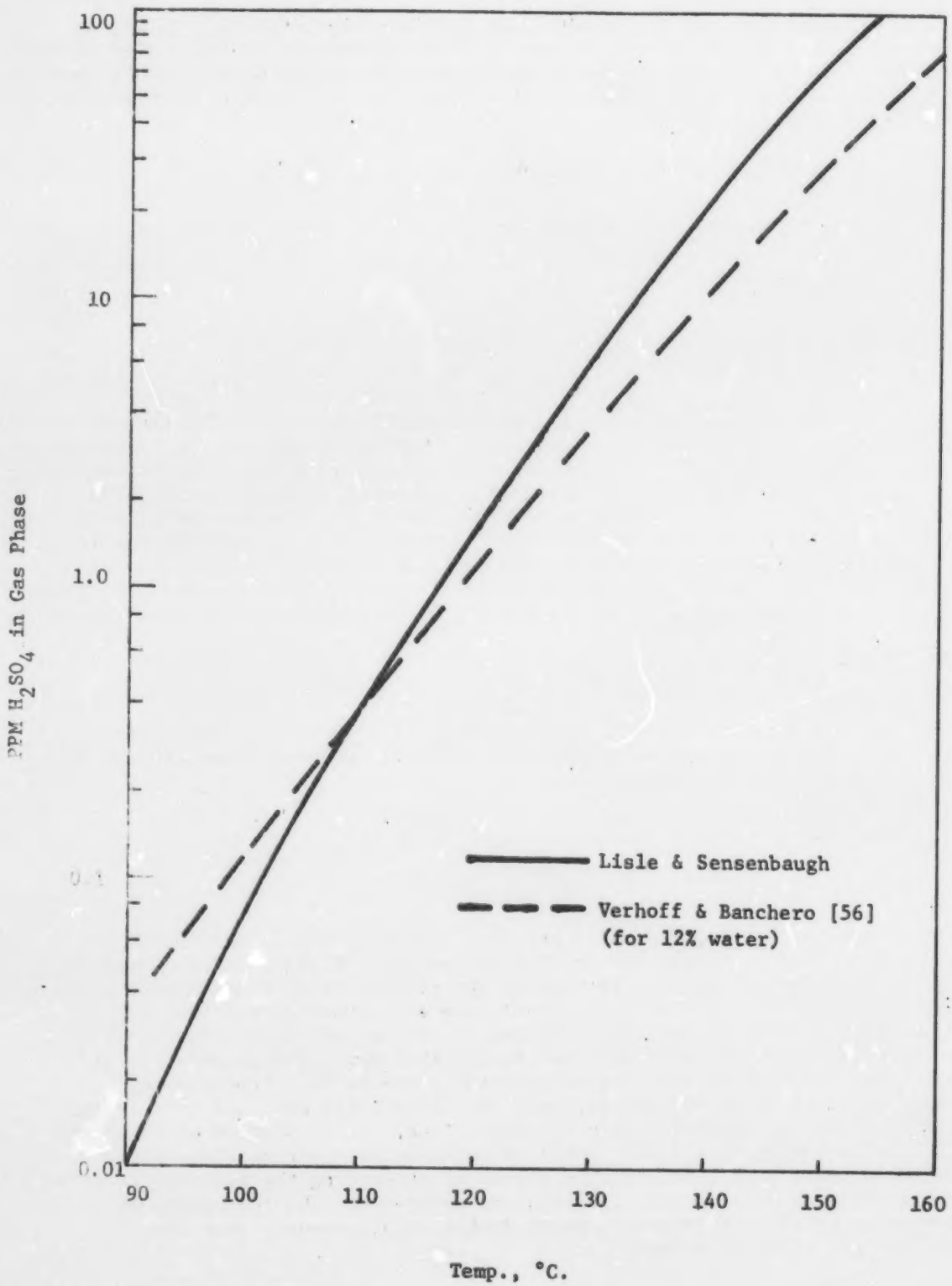


Figure 3

Dew Point of H_2SO_4(g)



II. Reaction of Sulfur Dioxide and Trioxide with Exhaust Gas Constituents and Exhaust System Components

There are several exhaust gas constituents and system materials with which the sulfur oxides can react. The two main exhaust gas constituents capable of reaction with sulfur dioxide and sulfur trioxide are ammonia and carbon monoxide, both of which are more basic than the sulfur oxides. The pertinent reactions are:

$$2NH_3 + SO_3 + H_2O \rightleftharpoons (NH_4)_2\,SO_4 \qquad (3)$$

$$2NH_3 + 3SO_3 \rightleftharpoons N_2 + 3H_2O + 3SO_2 \qquad (4)$$

$$SO_3 + CO \rightleftharpoons CO_2 + SO_2 \qquad (5)$$

$$2SO_2 + 4CO \rightleftharpoons S_2 + 4CO_2 \qquad (6)$$

The first reaction is thermodynamically unfavorable at exhaust temperatures and, further, any ammonia would be oxidized over the oxidation catalyst before reaction with the trioxide could take place. The second reaction is also very unlikely due to the oxidation of the ammonia. The reduction reactions by carbon monoxide are both favorable but most likely limited due to kinetics. The reactions of both sulfur oxides with the iron or aluminum oxide catalyst support are favorable. The aluminum oxide can alternately form the sulfate and decompose as the catalyst temperature cycles during transient driving modes producing a sulfate storage/release phenomena.

A. Reaction of Ammonia with Sulfur Trioxide

The free energies and equilibrium constants for Reaction 3 are given as functions of temperature in Table II. The thermodynamic equilibrium constant, given by the relationship

$$Kp = \frac{1}{\left(P_{NH_3}\right)^2 \left(P_{H_2O}\right) \left(P_{SO_3}\right)^3} \qquad (7)$$

for an exhaust gas containing 10 ppm NH_3, 12% H_2O, and 10 ppm SO_3 is 8.3×10^{15} atm^{-4}. Comparison of this value with the equilibrium constants in Table II shows that the reaction is favorable only at temperatures below 225°C. Since the equilibrium constants are such a strong function of temperature, order of magnitude changes in the concentration of either ammonia or sulfur trioxide will not appreciably alter the temperature at which the reaction becomes thermodynamically favorable. Temperatures below 225°C occur in the exhaust only at the tailpipe exit and only during start up and some extended idle periods. Thus, the production of ammonium sulfate in the exhaust system would be possible only during these modes. Ammonium sulfate may, however, be formed after exiting the tailpipe in either the atmosphere or a particulate sampling apparatus. The thermodynamic favorability of this occurence would depend simultaneously upon the cooling and dilution rates.

TABLE II

Free Energies and Equilibrium Constants for the Reaction of Ammonia and Sulfur Trioxide Forming Ammonium Sulfate [33]

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-4})
298	-63,830	6.18×10^{46}
400	-49,100	6.75×10^{26}
500	-34,900	1.80×10^{15}
600	-21,000	4.47×10^{7}
700	- 7,400	5.32
800	+ 5,800	2.60×10^{-2}

The possibility of ammonium sulfate production is most severe in catalyst equipped vehicles where the potential of forming sulfur trioxide is greatest. However, in these vehicles the oxidation of ammonia over the catalyst must be considered. The oxidation of ammonia over platinum to produce nitric oxide is a very important and well known industrial reaction [15]. The reaction is very rapid with almost complete oxidation.

TABLE III

Free Energies and Equilibrium Constants for the Reaction of Ammonia and Sulfur Trioxide to form Nitrogen, Water, and Sulfur Dioxide [33]

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{2})
298	-105,510	2.21×10^{77}
400	-114,100	2.22×10^{62}
500	-122,500	3.54×10^{53}
600	-131,000	5.26×10^{47}
700	-139,400	3.36×10^{43}
800	-147,700	2.25×10^{40}
900	-155,900	7.26×10^{37}
1000	-164,100	7.36×10^{35}

B. Reduction of Sulfur Trioxide by Ammonia

Reaction 4 illustrates a reaction mechanism whereby exhaust ammonia can be consumed. The equilibrium thermodynamics for this reaction are given in Table III. The extremely large equilibrium constants show that this reaction has the potential of almost complete removal of either the ammonia or the sulfur trioxide, whichever is initially present at lower concentration. Assuming that the reaction kinetics are sufficiently rapid, this reaction would then preclude the formation of ammonium sulfate.

Typical automotive exhaust without catalysts contains from one to six ppm ammonia depending upon driving mode with an average of 2.2 for a typical driving cycle [23]. Our results with the dual-catalyst system show that an active automotive oxidation catalyst will readily oxidize ammonia resulting in tailpipe concentrations typically less than 1 ppm. Therefore, even at low exhaust temperatures where ammonium sulfate formation is thermodynamically favorable, only small amounts could be made. This agrees with Ford Motor Company's finding [17] that little or no ammonium sulfate or bisulfate is found in automotive particulate.

C. Reduction of Sulfur Trioxide by Carbon Monoxide

Reaction 5 is a second possible reaction which would lead to a reduction in sulfur trioxide emissions. The equilibrium thermodynamics for this reaction, as given in Table IV, were calculated from data presented in the JANAF Thermochemical Tables [20]. The equilibrium constants indicate that, even for carbon monoxide concentrations in the ppm range, the reaction is favorable at exhaust gas concentrations. The extent of the reaction would, however, probably be limited by the reaction rate.

TABLE IV

Free Energies and Equilibrium Constants for the Reduction of Sulfur Trioxide by Carbon Monoxide

Temp (°K)	Free Energy (Cal/mole)	Equilibrium Constant (dimensionless)
500	-44,870	4.11×10^{19}
600	-45,020	2.51×10^{16}
700	-45,160	1.26×10^{14}
800	-45,310	2.39×10^{12}
900	-45,450	1.09×10^{11}
1000	-46,670	1.59×10^{10}

D. Reduction of Sulfur Dioxide by Carbon Monoxide

The last possible reaction is the reduction of sulfur dioxide to elemental sulfur by reaction with carbon monoxide. The thermodynamic data calculated from the JANAF Tables [30] are presented in Table V. The equilibrium constant for this reaction is written as,

$$Kp = \frac{P_{CO_2}^4}{P_{CO}^4 \, P_{SO_2}^2} \qquad (8)$$

In a pre-catalyst vehicle, typical exhaust consentrations would be $P_{CO_2} = 0.12$ atm, $P_{SO_2} = 2 \times 10^{-5}$ atm, and $P_{CO} = 0.01$ atm. At these levels, the reduction of sulfur dioxide by carbon monoxide would become favorable at temperatures below 600°C. In a catalyst vehicle the partial pressure of carbon monoxide would be typically less than 10^{-4} atm in which case the reaction would become favorable at temperatures less than 375°C. Hence, for both catalyst and non-catalyst vehicles, the reduction of sulfur dioxide to elemental sulfur is thermodynamically feasible within the exhaust system.

TABLE V

Free Energies and Equilibrium Constants for the Reduction of Sulfur Dioxide by Carbon Monoxide

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-2})
500	-73,390	1.21×10^{32}
600	-68,440	8.54×10^{24}
700	-63,560	7.01×10^{19}
800	-58,660	1.06×10^{16}
900	-53,800	1.16×10^{13}
1000	-48,540	4.07×10^{10}

E. Reaction of Sulfur Oxides with Iron

The most prevalent solid material with which sulfur oxides can react is the iron of the engine and exhaust system. Since the newer model cars and all future oxidation catalyst vehicles are operated net lean, either by carburetion or by air injection, the internal iron surfaces of the exhaust system will be oxidized. A typical iron-sulfur oxide reaction is the sulfation of ferric oxide by sulfur trioxide,

$$Fe_2O_3 + 3SO_3 \rightleftharpoons Fe_2(SO_4)_3. \qquad (9)$$

A similar type of reaction can also be written for sulfur dioxide where iron sulfite is the product. These types of reaction are industrially important in the corrosion of iron or steel surfaces in contact with flue or stack gases containing oxides of sulfur. In this vein, the sulfation of iron has been examined by several researchers [35, 36, 24]. Warner and Ingraham [58, 59] have also investigated the reverse reaction in their studies on the processing of metallic ores.

These studies as well as thermodynamic calculations, show that the sulfation of ferric oxide by sulfur trioxide in the concentration range of catalyst vehicles becomes favorable at temperatures below 450°C. Table VI contains the pertinent thermodynamic data. Therefore, sulfation is possible over a large fraction of the exhaust system. Furthermore, there will be a zone in which the temperature will oscillate, as the driving mode changes, around the temperature at which the reaction is favorable. It is therefore possible for this zone to either pick up or release sulfur oxides depending upon the temperature and sulfur oxide concentration.

TABLE VI

Free Energies and Equilibrium Constants for the Reaction of Sulfur Trioxide with Ferric Oxide

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-3})
500	-70,730	8.29×10^{30}
600	-57,790	1.13×10^{21}
700	-49,940	3.92×10^{15}
800	-32,170	6.15×10^{8}
900	-19,420	5.20×10^{4}
1000	- 6,720	2.94×10^{1}

Warner and Ingraham [59] allude to the mechanism of ferric sulfate decomposition. Their work with decomposition under atmospheres of varying sulfur dioxide and trioxide compositions indicates that the decomposition products are more likely to be sulfur dioxide and oxygen than sulfur trioxide.

Therefore, it is possible to store sulfate in the exhaust system by the reaction of sulfur trioxide with iron and then to release this stored sulfate as sulfur dioxide and oxygen.

The relative reaction rates of iron sulfation by sulfur dioxide and sulfur trioxide can be assessed from the work of Pechkovsky [34] and Krause et. al. [35]. Pechkovsky studied the reaction of sulfur dioxide with various metal oxides in an oxidizing environment. He showed that sulfation of some metals, notably magnesium oxide, was very slow with only sulfur dioxide present. When a small amount of catalyst, such as ferric

oxide, was added, the reaction proceeded much more rapidly presumably due to the oxidation of sulfur dioxide to the trioxide which then reacted more readily. Krause et. al. [35], using a radioactive tracer technique, found sulfur trioxide to be on the order of 10^4 times more reactive on a molar basis than the dioxide.

F. Reactions of Sulfur Trioxide with Aluminum Oxide

Another material in the exhaust system of a catalyst equipped vehicle with which sulfur trioxide can react is the aluminum oxide catalyst substrate via the reaction

$$Al_2O_3 + 3SO_3 \rightleftharpoons Al_2(SO_4)_3. \qquad (10)$$

The thermodynamic data for this reaction [33] are given in Table VII for gamma form of aluminum oxide. The equilibrium partial pressures for sulfur trioxide are also presented in this table. These data show that this reaction is favorable for typical sulfur trioxide exhaust gas compositions when the temperature is below 425°C. While no quantitive data are available on the kinetics of this reaction, qualitatively they are rapid enough to be significant as witnessed by the sulfate storage noted by several investigators [2, 18, 45].

TABLE VII

Free Energies, Equilibrium Constants, and Equilibrium Partial Pressures for the Reaction of Sulfur Trioxide with Gamma Aluminum Oxide

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-3})	Equilibrium Partial Pressure of Sulfur Trioxide (atm)
298.16	111,000	2.34×10^{81}	7.53×10^{-28}
400	96,900	8.87×10^{52}	2.24×10^{-18}
500	83,200	2.34×10^{36}	7.53×10^{-13}
600	69,900	2.91×10^{25}	3.25×10^{-9}
700	56,700	5.05×10^{17}	1.26×10^{-6}
800	43,800	9.25×10^{11}	1.03×10^{-4}
900	30,900	3.19×10^{7}	3.15×10^{-3}
1000	18,200	9.50×10^{3}	4.72×10^{-2}

The release of this stored sulfur can also play an important part in automobile sulfate emissions. As the above reaction indicates, the aluminum sulfate can decompose back to the oxide with the release of sulfur trioxide. Such a release would become thermodynamically favorable above 425°C. Wagner and Ingraham have examined the thermodynamics [58] and kinetics [59] of the decomposition of aluminum and ferric sulfates. As discussed above, they found that the rate of ferric sulfate decomposition was proportional to the sulfur dioxide driving force. That is to say that the decomposition favors the formation of sulfur dioxide rather than the trioxide. Although they did not investigate the mechanism of aluminum sulfate

decomposition, by analogy with ferric sulfate decomposition, aluminum sulfate could decompose into oxygen and sulfur dioxide. Thus, it could be possible for sulfur trioxide formed on the catalyst to react with the substrate only to be released later at a higher temperature as sulfur dioxide. With this possibility, care must be exercised in designing and interpreting experiments examining the fate of gasoline sulfur over an oxidation catalyst.

Kelley [33] presents an alternate route for aluminum sulfate decomposition in the presence of carbon monoxide. The reaction is

$$Al_2(SO_4)_3 + 3CO \rightleftharpoons Al_2O_3 + 3SO_2 + 3CO_2. \qquad (11)$$

The equilibrium constant for this reaction, $K^{1/3} = P_{SO_2} P_{CO_2} / P_{CO}$ is on the order of 3×10^9 atm for all temperatures. Since this equilibrium constant is very large, the partial pressure of carbon monoxide must be extremely small before this reaction becomes unfavorable. Thus this reaction may provide a route for sulfate release. Kelley feels that the actual mechanism of this reaction is the decomposition of aluminum sulfate to sulfur trioxide which is subsequently reduced to sulfur dioxide by carbon monoxide. He feels that the addition of carbon monoxide may reduce the decomposition temperature of aluminum sulfate by about 50°C.

III. Automotive Catalysis of Sulfur Dioxide

The only oxidation catalysts presently envisioned for automotive application are platinum and platinum-palladium catalysts. This section will therefore be limited to these catalysts. The bulk of the literature covering platinum oxidation of sulfur dioxide pertains mainly to use in sulfuric acid plants and, to a much lesser extent, in flue gas sulfur dioxide control. In these applications, the sulfur dioxide concentrations are much higher, 5-8% and 1% respectively, than found in typical automotive exhaust, 20 ppm. Even though the exhaust concentration is orders of magnitude below the percent level, the kinetic mechanism of catalysis over platinum should be the same. This suggests that the rate equations would also be valid. The first part of this section will review this literature. The second part will review the more limited, recent literature dealing directly with the sulfur dioxide oxidation over automotive catalysts.

A. Platinum Catalysis: Industrial Application

The use of platinum as a catalyst in the oxidation of sulfur dioxide was first disclosed in a patent by Peregrine Phillips in 1831. [41] This discovery is considered the foundation of the contact process for manufacturing sulfuric acid.

It wasn't until the 1900's that quantitative data became available concerning the rate and the mechanism of the oxidation reaction over various forms of platinum. This began with the classic work of Knietsch [34] in 1901. Knietsch examined the effect of space velocity and inlet concentrations on the conversion of SO_2 as a function of catalyst temperature. The catalyst consisted of 0.5 gm. of platinum supported on 5 to 10 gms. of asbestos. The oxygen concentration was held constant at 10% and 7 - 20% SO_2 concentrations were examined over the temperature range of 300 to 900°C. For this range of variables, conversions of from 0 to 99% were obtained. At a given space velocity, the experimental conversion was low at 300°C. As the temperature was increased, the conversion increased rapidly reaching a maximum in the temperature range of 400-500°C depending upon space velocity. Maximum conversions were in the range of 70 to 99% again depending upon space velocity. The lower space velocities peaked at lower temperatures and at greater conversions. As the temperature was increased further, the conversions decreased paralleling equilibrium with the lower space velocities nearer equilibrium. The limited data at the higher SO_2 level (20% instead of 7%) showed a decrease in conversion at identical temperature and space velocity. From these data, Knietsch duduced that the reaction rate was proportional to the concentrations of sulfur dioxide and oxygen [61] and is independent of the concentration of sulfur trioxide. The accuracy of these data have since been questioned due to Knietsch's poor temperature control and large conversions.

In another classical study of heterogeneous catalysis, Bodenstein and Fink [6, 7] investigated the oxidation of SO_2 over a platinum gauze of 0.06 mm diameter wire. This study, conducted over the experimental temperature range of 150-250°C, produced a reaction rate which is proportional to the first power of the sulfur dioxide concentration and inversely proportional to the square root of the sulfur trioxide concentration for the case where $C_{SO_2}/C_{O_2} = 3$. Where this ratio is greater than 3, the reaction rate is proportional to the first power of the oxygen concentration and inversely proportional to the square root of the sulfur trioxide concentration. The usefulness of these rate equations is, however, somewhat limited due to the very low temperatures investigated.

Lewis and Ries,[37,38] objecting to the poor control of experimental conditions by Knietsch and to Bodenstein's low temperature range, obtained catalytic data under carefully controlled conditions approximating actual contact plant operations. Their kinetic experiments were designed and conducted so as to approximate a differential reactor, that is, a reactor in which the conversion is allowed to change only to a small extent. Thus, the reaction is taking place throughout the reactor with approximately the same reactant and product concentrations. In addition, the temperature does not change due to reaction exo- or endothermicity since conversions are differential. This is the classically accepted method for obtaining accurate kinetic data.

Lewis and Ries performed three separate series of tests. In the first series the effect of inlet sulfur dioxide concentration was examined by varying the amount of sulfur dioxide in an air-sulfur dioxide feed. In the second series, the amount of oxygen was varied by dilution of the air-sulfur dioxide feed with nitrogen. The final series examined the effect of sulfur trioxide on the reaction kinetics. For this series, a platinum preconvertor was used to generate feeds with varying sulfur dioxide and trioxide concentrations.

An attempt was then made to fit these data with an equation obtained directly from the law of mass action

$$r = k(SO_2)^2\, O_2 - \frac{(SO_3)^2}{Ke} . \qquad (12)$$

This equation, which they found to fit Knietsch's data, would not fit their data. They then tried Bodenstein's equation,

$$r = k\, SO_2/SO_3^{\,1/2} \qquad (13)$$

which was somewhat better than the law of mass action but still incapable of interpreting the data. Several other forms of rate equations were tried with the best results being obtained with the form

$$r = k\, P_{SO_2} \ln \frac{P^e_{SO_3}\, P_{SO_2}}{P_{SO_3}\, P^e_{SO_2}} ; \qquad (14)$$

where the superscript e denotes the equilibrium partial pressure. This rate equation also correlates the data of Bodenstein and Fink better than the rate equation proposed by Bodenstein and Fink.

Unfortunately, as pointed out by Uyehara and Watson [55], the total amount of platinum used by Lewis and Ries was not determined. The amount used was constant for all of the experiments making the rate data consistent. However, it is impossible to derive absolute reaction rate constants since the amount of catalyst is unknown.

Taylor and Lenher [54] used a static platinum hot-wire technique to examine the approach to equilibrium from both sides at a temperature of 665°C. They found that the following rate equation best represented their data

$$r = k_1 \frac{P_{SO_2} - P^e_{SO_2}}{P_{SO_3}^{1/2}} - k_2(P^e_{SO_3} - P_{SO_3}) \qquad (15)$$

In 1937, Salsas Serra [50] examined the experimental work of Knietsch and Bodenstein and Fink in light of the law of mass action. In opposition to the findings of Lewis and Ries discussed above, he found

that the law of mass action adequately represented these data. The law of mass action for the oxidation of sulfur dioxide yields the following rate equation,

$$r = k_1 P^2_{SO_2} P_{O_2} - k_2 P^2_{SO_3} . \qquad (16)$$

Hougen and Watson [20] developed general rate equations for heterogeneous catalysis where one of the elementary reaction steps in the overall series of steps is assumed to be rate controlling. In general, the elementary reaction steps, neglecting mass transfer steps, of the general reaction of A + B to produce C are:

1. The adsorption of either or both reactants on the catalyst surface.

2. The reaction of A + B either both as absorbed species or as one absorbed specie and one gaseous specie.

3. The desorption of the produce from the catalyst surface.

Assuming that one of these steps is rate controlling, i.e., much slower than the other steps, while the remaining steps are at equilibrium, a general rate equation can be written for each case. Uyehara and Watson, in a companion paper [65], applied this procedure to the catalytic oxidation of sulfur dioxide. The data of Lewis and Ries were selected for analysis since they were obtained in an apparatus reasonably resembling a differential reactor. The data of Knietsch, Bodenstein and Fink, and Taylor and Lenher were unsatisfactory since they were all obtained in static systems in which concentration and temperature gradients were present. Uyehara and Watson examined each possible rate limiting case and determined that the limiting step is

$$r = \frac{k_1 \left(P_{SO_2} P_{O_2}^{1/2} - \frac{P_{SO_3}}{K_e}\right)}{\left(1 + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{SO_3} P_{SO_3}\right)^2} \qquad (17)$$

where K_{O_2} and K_{SO_3} are the absorption equilibrium constants for oxygen and sulfur trioxide respectively. It should be noted that Uyehara and Watson have dropped the sulfur dioxide absorption term from the denominator of the general rate equation. Based on Lewis and Reis' first experimental series looking at the effect of sulfur dioxide concentration, Uyehara and Watson concluded that this absorption term is negligible. Expressions for the coefficients appearing in this equation were updated by Hougen and Watson [25] by the inclusion of Hurt's data [28]. Since the mass of Hurt's catalyst was known, an absolute rate constant could be determined. These coefficients are:

$$k_1 = \exp\ -\frac{8,000}{T} + 14.154\ , \tag{18}$$

$$K_{O_3} = \exp\ \frac{20,360}{RT} - \frac{23.0}{R}\ , \text{ and} \tag{19}$$

$$K_{SO_3} = \exp\ \frac{16,800}{RT} - \frac{17.51}{R}\ . \tag{20}$$

Boreskov [8] found that the data of Bodenstein and Fink, Taylor and Lenher and Pligunov (unpublished) agreed very well with the rate equation

$$r = k, \frac{P_{SO_2}\ P_{O2}^{0.25}}{P_{SO_3}^{0.5}} - k_2 \frac{P_{SO3}^{0.5}}{P_{O_2}^{0.25}} \tag{21}$$

He further states that this equation can be accounted for by assuming that the rate limiting step is the absorption of SO_2 on the catalyst. This equation was also successfully used by Chesalov and Boreskov [11,12] in the study of catalytic activity of various platinum catalysts.

Roiter et.al [47] examined the oxidation near equilibrium of sulfur dioxide over a platinum screen by means of a tracer technique using a radioactive sulfur isotope. The kinetics were also examined under nonequilibrium conditions using a standard static measurement technique. The experimental temperature ranged from 600 to 674°C while the initial sulfur dioxide level ranged from 2.7 to 6.3%. The data were then fit to the Boreskov equation with large descrepancies being noted. A rate equation was then developed assuming that the rate determining step is the surface reaction of adsorbed oxygen and sulfur dioxide

$$r = k\ P_{SO_2}\ P_{O_2}^{1/2} - \frac{P_{SO_3}}{K^e} \tag{22}$$

This rate equation agreed quite well with the data under equilibrium and nonequilibrium conditions.

At this point in the historical review, it is instructive to examine some of the common features of the studies and rate equations reported. One important experimental aspect, which is particularly germane to actual large-scale reactors such as on vehicles, is the neglect of mass transfer effects in the analysis of the data. This neglect of mass transfer may be responsible for the difference in rate equations. For convenience Table VIII summarizes the rate equations and pertinant experimental conditions. The effect of mass transfer has been examined in more recent literature and will be discussed later.

All of the rate equations, with the exceptions of Bodenstein and Finks second equation and Salsas Serra's equation, predict that the

TABLE VIII

SUMMARY OF RATE EQUATIONS FOR PLATINUM CATALYSIS OF THE OXIDATION OF SULFUR DIOXIDE

Investigator	Rate Equation	Catalyst Description	SO_2 Range	O_2 Range	Conversion Range	Temp. Range
Knietsch [34]	$r = k_1 P_{SO_2} P_{O_2}$	Pt on asbestos	7% + 2-%	10%	0-99%	300-900°C
Bodenstein and Fink [6,7]	$r = k_1 P_{SO_2} P_{SO_3}^{-0.5}$	Pt mesh, 0.06mm diameter		P_{SO_2}/P_{O_2} <3		150-250°C
Bodenstein and Fink [6,7]	$r = k_1 P_{O_2} P_{SO_3}^{-0.5}$	Pt mesh, 0.06mm diameter		P_{SO_2}/P_{O_2} >3		150-250°C
Lewis and Ries [37,38]	$r = k_1 P_{SO_2} \ln \frac{P^e_{SO_3} P_{SO_2}}{P^e_{SO_2} P_{SO_3}}$	7% Pt on asbestos	<0.5%	air		400-450°C
Taylor and Lenher [54]	$r = k_1 (P_{SO_2} - P^e_{SO_2}) P_{SO_3}^{-0.5} - k_2 (P^e_{SO_3} - P_{SO_3})$	Pt wire				525-700°C
Salsas Serra [50]	$r = k_1 P^2_{SO_2} P_{O_2} - k_2 P_{SO_3}^2$ (Analysis of Knietsch [K-8] and Bodenstein [B-4,5]					
Uyehara and Watson [55]	$r = \frac{k_1}{(1 + P_{O_2}^{0.5} K_{O_2}^{0.5} + P_{SO_3} K_{SO_3})^2} (P_{O_2}^{0.5} P_{SO_2} - \frac{P_{SO_3}}{Ke})$	(Analysis of Lewis and Ries data [L-4,5] with inclusion of Hurt data) [H-8]				
Boreskov [8]	$r = k_1 P_{SO_2} P_{O_2}^{0.25} P_{SO_3}^{-0.5} - k_2 P_{O_2}^{-0.25} P_{SO_3}^{0.5}$	Pt wire				530-850°C
Roiter et al. [47]	$r = k P_{O_2}^{0.5} P_{SO_2} - \frac{P_{SO_3}}{Ke}$	Pt screen	1-3%	~19	0-100%	420-700°C
Olsen et al. [42]	$r = (P_{SO_2} P_{O_2}^{0.5} - \frac{P_{SO_3}}{Ke}) (B + D P_{SO_3})^{-2}$	0.2% Pt on 1/8 alumina pellets (50,000 v/v/hr.	6.45%	air	4-70	350-480°C

forward reaction rate is proportional to the first power of the sulfur dioxide partial pressure. The functional dependency on the oxygen partial pressure is somewhat less clear. Several of the early equations are independent of oxygen partial pressure, however, in these cases the experimental oxygen levels were in large excess. The experimentally small concentration changes due to reaction were almost insignificant in comparison with the large unreacted excess. This and other experimental inaccuracies yielded equations which were independent of oxygen effects. Such was the case of Lewis and Ries' data and analysis. Later analysis of these data by Uyehara and Watson did however show an oxygen dependency proportional to the square root of the oxygen partial pressure. This same oxygen functionality was also determined by Roiter where various oxygen concentrations were examined.

In essentially all of the experimental work, a marked reduction was noted with the presence of even very small amounts of sulfur trioxide. Two methods of accounting for this retardation were used in the development rate equation. The first method was to place the sulfur trioxide partial pressure in the denominator of the forward reaction rate term. The second method was to include a reverse-reaction term in the rate equation such as exemplified in the Uyehara and Watson and Roiter equations. The second method also provides mathematical tractability in that the rate can go to zero as equilibrium is approached. The first method, see for instance the equation of Bodenstein and Fink or Lewis and Ries, does not account for equilibrium conditions and, therefore, would be unacceptable.

Of the equations discussed, the best with respect to data representation, mathematical formulation and generality is that of Uyehara and Watson. This equation has the general form of the law of mass action and represents the reliable differential reactor data of Lewis and Ries quite well. In addition, the absolute rate constants are available where they are not for several of the other equations.

The effect of diffusion on the overall sulfur dioxide conversion of a large-scale reactor can be determined from the work of Hurt [28] Hurt used the oxidation of sulfur dioxide over platinum as an example of his procedure for correlating the performance of small-scale with large scale reactors. An estimate of the influence of mass transfer on the overall sulfur dioxide conversion in a GM reactor can be made using Hurt's kinetic data and mass transfer correlations.

At 40 mph cruise conditions, a typical superficial mass velocity would be 248 $lb/hr\text{-}ft^2$. This represents a particle Reynolds number of 30 for 1/8" pellets. Using Hurt's kinetic correlation and mass transfer correlation, the overall conversion is influenced approximately 25% by mass transfer and approximately 75% by kinetics. Although these values may be in error due to kinetic differences in Hurt's catalyst and automotive catalysts, it does illustrate that

mass transfer effects can play a significant role in the formation of automotive sulfates. It also points out that care should be exercised in designing and analyzing kinetic experiments particularly when the goal of the experiment is to predict large-scale reactor behavior from small-scale reactor experiments.

Smith et al. [1, 22, 29, 42, 52] completed a very comprehensive program involving the design of fixed bed catalytic reactors taking into account heat and mass transfer. The program involved measurement of the chemical kinetics in a differential reactor, examination of diffusional effects, examination of heat transfer effects, and mathematical modeling of an integral reactor incorporating kinetics and heat and mass transfer. The results are of particular interest since the reaction used was oxidation of sulfur over a catalyst of 0.2 weight percent platinum on 1/8" alumina pellets. The platinum was applied such that it penetrated only the outer 1/32" of the pellet. This platinum loading and geometry approximates that of the GM catalyst. In addition, the range of temperature and space velocities spans the range of interest in automotive applications. However, the sulfur dioxide levels were constant and typical of acid plant operations, 6%, and the oxygen levels were those of air. Thus, the only variable investigated was conversion. Overall conversions up to 70% were examined in one paper by using a preconverter ahead of the differential reactor [42]. The maximum conversion over the differential reactor was in all but two cases less than 30%.

Olsen et al. [42] chose to model their results with the rate equation of Uyehara and Watson [55]. Since the inlet concentrations to the preconverter were always the same, there existed a definite relationship between P_{SO_2}, P_{SO_3}, and P_{O_2}. Therefore, the Uyehara and Watson equation could be simplified, using the relationship, to

$$\frac{P_{SO_2} P_{O_2}^{1/2} - \frac{P_{SO_3}}{K}}{r}^{1/2} = B + D P_{SO_3}, \qquad (23)$$

where B and D are constants dependent only upon temperature. Olsen, et al. found that this equation was an excellent representation of their data when the component partial pressures were taken at their interfacial values and not their bulk values, that is to say that diffusion is taken into account.

In a later paper of this series, Argo and Smith [1] obtained differential reaction rates using larger catalyst pellets than Olson, 1/4" in place of 1/8". These data were then correlated with the Olson data by an activity factor in conjunction with the rate equation of Olson. The activity factor and rate equation correlated both sets of data very well again illustrating that this general equation is capable of describing the catalytic oxidation of sulfur dioxide by platinum.

Olson also examined five other rate controlling mechanisms. The data were correlated by rate equations derived from the following rate limiting elementary steps:

1. Reaction of adsorbed sulfur dioxide and adsorbed oxygen (this mechanism yields the Uyehara and Watson rate equation),

2. Reaction of adsorbed sulfur dioxide with gas-phase molecular oxygen, or

3. Reaction of adsorbed oxygen and gas phase sulfur dioxide.

Unfortunately, the data could not distinguish among these three steps. The data were, however, not correlated by any mechanism which assumes that adsorption or desorption is the rate limiting step.

The differential reaction data were also analyzed by Hurt's [28] method which also accounts for the effect of diffusion. This method failed to correlate the data with the primary objection being that the resistance due to reaction at the catalytic surface was not independent of mass velocity. Olson found that the diffusional effects were better accounted for by using the mass-transfer correlations of Hougan and Wilkie [20]. Using these correlations, differences in the sulfur dioxide and trioxide partial pressures between the bulk gas and the catalytic surface were as great at 40% depending upon gas mass velocity, degree of conversion, and temperature. For a GM reactor running at 40 mph, partial pressure differences on the order of $\sim$ 10% would be predicted for both sulfur dioxide and trioxide. Therefore, this treatment in qualitative agreement with Hart's method indicates that mass transfer can be playing a role in the production of sulfuric acid over the GM type of automotive catalyst.

The mechanism of the oxidation of sulfur dioxide over platinum was examined by Kaneko and Okanaka [31,32] using a radioactive tracer technique. The experiments were conducted near 400°C in a recirculating reactor using a platinum gauze catalyst of 0.1 mm diameter wire. The kinetic mechanism was examined on both sides of equilibrium, i.e. oxidation of sulfur dioxide and decomposition of sulfur trioxide. The reaction mixture contained only oxygen, sulfur dioxide, and sulfur trioxide with the oxygen and sulfur dioxide always in stoichiometric amounts. In one series of experiments, radioactive sulfur was used to follow the reaction. In the second series an isotope labelling of oxygen was employed. The combined results of both series show that the rate-determining step is the surface reaction of adsorbed oxygen and adsorbed sulfur dioxide.

In summary, the literature covering the mechanism of sulfur dioxide catalysis by platinum indicates the rate limiting step is the surface reaction between adsorbed oxygen and adsorbed sulfur dioxide.

The rate equation which produced the best representation of experimental data was that of Uyehara and Watson[55] which is in agreement with the above rate controlling mechanism. Most of the other rate equations are special cases of the more general Uyehara-Watson equation which further substantiates its validity.

There are two interesting points which deserve mention when applying this rate equation to the area of automotive sulfuric acid production. First, since the rate equation is first order with respect to sulfur dioxide partial pressure, the sulfuric acid production will be linearly proportional to the fuel sulfur level. The second important point addresses the problem of controlling acid emissions. Since the rate equation is proportional to the square root of the oxygen partial pressure, catalytic systems which operate with lower oxygen partial pressures will produce lower sulfuric acid emissions. Thus, a catalytic system, such as the three-way catalyst, which operates with no net oxygen partial pressure would minimize acid emissions.

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Platinum Catalysis: Automotive Application

Although the literature is void of reaction rate and reaction mechanism studies which relate directly to exhaust oxidation of sulfur dioxide, there are several references covering phenomenological observation of the catalysis of exhaust sulfur dioxide. Chrysler [13], Ethyl [16], Ford [17], and General Motors [18] have made public their data on sulfate emissions as requested in the March 8, 1974 Federal Register. In addition, Pierson et al. [45] and Beltzer et al. [2] have presented SAE papers dealing with automotive sulfate emissions. All of these references, with the exception of General Motors, have examined platinum catalysis only from the standpoint of tailpipe emissions of sulfuric acid. General Motors has conducted a limited amount of laboratory work aimed directly at elucidating the kinetics.

In reviewing these references, there is, for the most part, a common problem when catalysts are employed in not being able to obtain a balance between the sulfur burned in the fuel and the sulfur emitted from the tailpipe. When catalysts are not used, balances can be obtained. Recently, however, some investigations have had problems in closing a sulfur balance on non-catalyst vehicles. Since the majority of the tailpipe sulfur in a non-catalyst vehicle is sulfur dioxide and a sulfur balance can be made, the analytical and test procedures for sulfur dioxide can be assumed to be valid and accurate. The ability then not to be able to close a sulfur balance on a catalyst vehicle is due either to an experimental or analytical problem or to the storage phenomena discussed previously. This problem makes it difficult to assess quantitative catalytic effects from observed tailpipe emissions.

Ford [17, 45] has been able to make sulfur balances for Englehard IIB-catalyst and non-catalyst vehicles operating under steady cruise conditions. They found that at 60 mph both the Engelhard IIB and GM catalysts converted approximately 44% of the sulfur dioxide to trioxide which is close to the equilibrium conversion at the test conditions. The GM catalyst at 30 mph converted 84% of the sulfur dioxide which is again very close to the equilibrium value. These conversions were all calculated on the basis of total sulfur out of the tailpipe, thus eliminating the storage problem noted with the GM catalysts.

Ethyl Corp. [16] found that under 40 mph cruise testing monolithic platinum catalysts converted 43% of the fuel sulfur to exhaust sulfate where conversion is based on total sulfur emitted. Their tests showed that approximately 58% of the fuel sulfur was emitted with the rest being stored. This conversion cannot be compared with equilibrium since the catalyst temperature was not given. The magnitude of these results are in line with Ford's findings.

Beltzer, et al., [2] have also measured sulfate emissions for steady cruise conditions. Sulfur dioxide measurements were not made precluding making a sulfur balance. The sulfate emissions at 60 mph

for the pelletized oxidation catalyst agree fairly well with those obtained by Ford using approximately the same fuel sulfur level. If the storage effects are similar then by implication, this conversion is also close to equilibrium.

The GM [18] extended 60 mph cruise tests on their catalysts show a large spread both in sulfate conversion and in sulfur balances. In general, average conversions based on sulfur emitted were in the range of 20 to 40%. This is somewhat lower than the conversions discussed above, but still represents a significant approach to equilibrium.

The Chrysler reference [13] did not present conversion data for steady cruise conditions. A consensus of these references shows that the reaction rate is of sufficient magnitude that the oxidation of the exhaust sulfur dioxide approaches equilibrium in actual vehicle operation. Due to the storage effect together with possible analytical problems, a more quantitative assessment of the reaction rate is impossible.

In addition to their vehicle work, GM [18] also reported some preliminary parametric studies using a laboratory-scale reactor. They also caution the reader that the analytical methods caused significant uncertainties in the sulfur trioxide measurements. The storage problem was also a large factor. In one instance less than 30% of the inlet sulfur could be accounted for.

GM examined the conversion both as a function of temperature and space velocity using actual vehicle exhaust. They found that the conversions, based on measured sulfur trioxide and average sulfur input, were between 5 and 15% with only a weak temperature dependency. From analysis of these data, with respect to temperature and space-velocity dependency, it was concluded that the reaction is kinetically controlled. The effect of platinum loading was also investigated by increasing the loading from 0.1% to 1.0% platinum. The observed effect was only a very slight increase in measured sulfur trioxide. This finding is in contradiction to a kinetically controlled reaction. If the reaction were kinetically controlled for both loadings, then an order of magnitude change in platinum loading would change the rate by an order of magnitude. Invariance to loading conforms with either a diffusion or equilibrium controlled reaction.

It is informative to examine these data assuming that the outlet sulfur trioxide is the difference between the outlet sulfur dioxide and the total inlet sulfur. This assumption could be valid if the sulfur trioxide analyses were in error and no storage was taking place. Under this assumption, the conversions are all very near equilibrium indicating that the reaction is equilibrium controlled. Some credibility must be assigned this probability since GM's platinum loading data also indicate an equilibrium controlled reaction. However, since the storage problem is real and the data severely limited, this assumption may not be entirely valid. None the less, the possibility exists that more sulfur dioxide is being produced than the GM data indicate.

The form of the rate equation describing the catalysis reaction can, to a limited extent, be deduced from the above studies. The results of Beltzer, Ford, and GM show that sulfate emissions increase with gasoline sulfur level. Beltzer and Ford find that conversion appears to be invariant with respect to fuel sulfur level which means the reaction rate is proportion. to the first power of the sulfur dioxide partial pressure in agreement with the rate equations previously discussed. The quantitative effect of oxygen partial pressure can be assessed from GM's vehicle and laboratory studies. These studies show that reducing the partial pressure of oxygen over the catalyst reduces sulfate emissions and the reaction rate. The quantitative dependency on the reaction rate cannot be determined due to the limited data of dubious accuracy.

In summary, the use of a platinum automotive-exhaust catalyst does result in oxidation of fuel sulfur to yield sulfur trioxide. The extent of this oxidation is clouded by the problems of sulfur storage and inaccurate analytical techniques. Results showing anywhere from 10% to complete approach to equilibrium have been observed. The variability of these data precluded any quantitative analysis of the reaction rate, however, the data did indicate the form for the reaction-rate equation. The rate equation should be linear with respect to sulfur dioxide partial pressure and should be proportional to some positive power of the oxygen partial pressure. This form is in agreement with the rate equations obtained in the industrial catalysis section.

IV. Sulfate Trap

There are two conceivable means of removing the sulfuric acid from a vehicle's exhaust system. The first is by the use of particulate traps in which the condensed acid is removed as droplets. The second is by reaction of the acid either as sulfur trioxide, gaseous sulfuric acid, or condensed, liquid sulfuric acid with a suitable sorbent. The capacity of either type of trap can be conservatively estimated for 50,000 miles by assuming an overall fuel economy of 10 miles per gallon. If the fuel sulfur level is taken as the industry average of 0.03 weight percent, and it is assumed that the worst possible case of total conversion exists, then 4.2 kgm or 131 gm. moles. of sulfur will be consumed and must be trapped.

The particulate trapping technique has several serious problems associated with it which preclude its use in automotive applications. The sorbent trap method is more attractive. Consideration of several important properties which a sorbent material must process shows that the most promising sorbent material is calcium oxide. Other attractive sorbents are the oxides of magnesium, manganese, and aluminum.

A. Particulate Trap

There are several very serious problems associated with collecting these sulfuric acid emissions with a particulate trap. The largest problem is that the sulfuric acid exits the tailpipe in the gas phase for the majority of driving conditions. This has been discussed previously. Therefore, for a particulate trap to be feasible, an exhaust heat exchanger would be required. Assuming condensation is possible, then the condensed acid must be separated from the exhaust gas by some means. This separation will be exceedingly difficult due to the extremely small particle size of the condensed acid. Typically, the particle sizes for the effluent of acid plants is less than 2 microns for 85 to 90% of the acid by weight [53] Ford [17] found that >90% of the exhaust sulfate mass was less than 0.25 microns. The problems associated with this separation would be almost unsurmountable given the space limitations and low back-pressure requirement. Assumi these problems can be overcome, the problem then becomes one of containing the liquid acid. Assuming the acid would be diluted by 50 weight percent water, the volume of acid solution collected over 50,000 miles would be 18.5 liters. Not only must this be contained, it must be protected from further dilution with water during cold starts and shut downs. Based on all of these problems, it is not feasible to use particulate traps to remove automotive sulfate particulate.

B. Sorbent Trap

The second method of reducing exhaust sulfate particulate is to trap the sulfur trioxide or sulfuric acid by chemical reaction with a solid sorbent material. In this manner, the potential sulfate particulate is trapped and stored in the exhaust system as a solid material. The obvious sorbents to consider for this application are solids which are chemically basic. While there are only a few references in the literature concerning the reaction of basic materials with either sulfur trioxide or gaseous sulfuric acid, there are numerous references to reactions with sulfur dioxide. The majority of these references are concerned with the selection of potential sorbent materials for the

reaction of either oxide is a gaseous acidic component reacting with a basic solid component and since the trioxide or gaseous acid is more acidic than the dioxide, then it would be expected that suitable sulfur dioxide sorbents would also serve as suitable trioxide sorbents. In fact, several researchers [3, 44] have found that the reactivity of the trioxide is orders of magnitude greater than that of the dioxide. Thus, the literature of sulfur dioxide removal will be used as a basis for selecting potential sulfate trap sorbents.

In selecting potential sorbents for automotive exhaust application, there are several important factors which must be considered. These factors are, 1 - activity for sulfur trioxide or sulfuric acid removal, 2 - thermal stability, 3 - volume and weight restrictions, 4 - potential side reaction, 5 - water solubility, 6 - cost and availability of sorbent, and 7 - toxicity of fresh or sulfated sorbent. The importance of the first factor goes without saying, a sorbent must be able to sorb over the temperature range encountered in automotive exhaust . The thermal stability of the sulfated sorbent is also vital to potential sorbents. The sulfated sorbent must not begin to decompose at temperatures below the maximum expected operating temperature of the catalyst. With this restriction, sulfated sorbents which decompose at temperatures below 800°C will not be considered.

Since the sulfate trap must be located in the exhaust system on the underside of the vehicle where space is limited volume and weight restrictions are important. Another important factor to consider in the selection of sorbent materials is the possibility of side reactions with exhaust gas constituents such as water or carbon dioxide to form stable compounds. Such reactions would use potential sulfate sorbent and decrease the sulfation capacity of the trap.

The water solubility of the fresh and sulfate sorbent material must be considered. There are several conditions in which part or all of the sulfate trap could be exposed to liquid water. If the sorbent is appreciably soluble, then the potential sulfate capacity can be decreased. This leaching of material can also lead to problems in maintaining the structural integrity of some possible trap configurations.

Since a successful sulfate trap has the possibility of being installed on millions of vehicles, the cost and availability of the sorbent must be considered. Thus, expensive metals such as gold or silver or materials available in limited quantities such as various rare earth elements cannot be considered.

Since the trap represents a potential source of particulate emissions due to fresh or sulfated sorbent attrition, the toxicity of the fresh and sulfated sorbent as well as other possible sorbent compounds must be considered. For instance, beryllium would be ideal from the volume-weight aspect due to its low molecular weight and divalency. However, it and its compounds are extremely toxic [51] and, hence, cannot be considered as potential sorbents.

With these factors in mind, the literature has been reviewed to select possible candidate sorbents to be used in a vehicle sulfate trap. There are several comprehensive references [8, 4, 21, 40 44, 59, 60] in the literature in which a wide variety of potential sulfur dioxide sorbents have been examined. These studies were all aimed at removing sulfur dioxide in the concentration range of 1 to 5 percent from a stack gas. Although these studies are for a higher concentration and a different oxide of sulfur, the activity results can be readily extrapolated to the sorption of sulfur trioxide from automotive exhaust.

The major chemical classification of the sorbent compounds investigated are the metal oxides. The sorbent material is envisioned as being installed in the system either as the oxide or as the metal which will readily oxidize in the oxidizing exhaust atmosphere. The general sorption reaction can be written as

$$MeO + SO_3\ (g) \longrightarrow Me\ SO_4 \qquad (24)$$

where Me is a general symbol representing any sorbent metal. Lowell, et al. [40] evaluated the oxides of 47 elements for potential use as sulfur dioxide sorbents. Their thermodynamic calculations show that the formation of sulfates for nearly all of the elements considered is favorable. Pechkovsky [44] examined the rate of sulfation of several metal oxides in powder form over a temperature range of 400-1000°C. He found that calcium oxide was more active than magnesium oxide which was more active then zinc oxide.

The Bureau of Mines [4] conducted a program looking at the activity of several bulk oxides with respect to their ability to sorb sulfur dioxide. Experimentally, a bed of sorbent, 8-24 mesh particles, was exposed to a synthetic flue gas with 0.3 volume percent sulfur dioxide. The space velocity was maintained at 1,050 v/v/hr and temperatures of 130 and 330°C were examined. Typical results showed that active sorption materials would remove essentially all of the sulfur dioxide for a period of time. As sulfation of the sorbent proceded, a point was reached where breakthrough would occur. From this point, the fraction of sulfur dioxide removed was found to decrease linearly with time.

The sorbent materials were rank ordered with respect to the amount of sulfur dioxide removed per unit mass of sorbent at the point of 90% removal of sulfur dioxide. The most active sorbents in order of activity were the oxides of manganese, cobalt, and copper.

The temperature study showed that for most sorbents approximately twice as much sulfur dioxide had been sorbed up to the 90% breakthrough point at 330°C than at 130°C. At the higher temperature, it was also noted that the sulfur dioxide had made a significant penetration into the particles of the more active sorbent materials.

Vogel, et al. evaluated the activity of several metal oxides supported on alumina. All test samples were made with the same metal equivalents so the various materials could be directly rank ordered as to activity. Samples of each supported sorbent were exposed to a synthetic stack gas and the outlet was continuously analyzed for sulfur dioxide. From these data, the sulfate loading of each sorbent was determined for the conditions where the outlet sulfur dioxide concentration was five percent of the inlet concentration. In addition, the maximum loading was determined by extrapolation of the data.

The materials were then rank ordered as to the percent of sorbent reacted at the five percent breakthrough point. This ranking also agreed with the ranking based on percent of sorbent reacted at maximum sulfation capacity with one exception. The one exception was the Bureau of Mines alkalized alumina sorbent which was included in this study as a benchmark. This material has been extensively studied [4, 5, 43, 40] as a sulfur dioxide sorbent but would not be acceptable as a vehicle trioxide sorbent due to its low sulfation capacity per unit volume.

The activity of the sorbents in order of decreasing activity is: the oxides of sodium, strontium, copper, calcium, and chromium. All of these materials had in excess of 50% of the sorbent reacted at the 5% breakthrough point. These were followed by the oxides of: barium, lead, cadmium, manganese, magnesium, iron, cobalt, nickel, and zinc. Tin and vanadium oxides showed no apparent activity. The alumina substrate was also tested and found to be completely inactive. In general, these results show that the alkali and alkaline earth metals exhibit highest reactivities. In addition, copper and chromium showed good reactivity.

Welty [60] conducted a theoretical study of the reactivity of potential sorbent cations based on a characterization factor consisting of the cation radius, electronegativity, and valence. Using this factor, the alkali metals are the most promising sorbents followed by the alkaline earth metals, then by various transition metals. This reactivity scale is in general accord with the experimental and theoretical works described previously.

The second necessary property a sorbent must have is thermal stability of the sulfated material. Although the temperature regime the sorbent sees in vehicle use can to some extent be controlled by location in the exhaust system, the sulfated material must have a higher decomposition temperature than it is expected to experience. Temperatures at or near the exit of the exhaust pipe can be as high as 800°C under sustained high speed driving of vehicles equipped with oxidation catalysts. Therefore, the sulfated sorbent must have a decomposition temperature at or above 800°C.

Table IX lists the decomposition temperatures of several sulfated sorbents. The temperature ranges and slight disagreement between references are due to the difficulty in experimentally determining decomposition temperature and in the different experimental methods employed. These results show that the sulfated alkali and alkaline earth metals all show acceptable decomposition temperatures. The transition metals, however, show borderline temperatures, particularly aluminum oxide. If these materials are to be considered, their installation would have to be limited to points as far from the oxidation catalysts as practical.

As estimated above, the sulfate trap must have the capacity to react with 131 gm. moles. of sulfur. Table X lists the mass of typical sorbents which would fulfill this requirement. In addition, the volume of sorbent as calculated using the crystalline density is included. In the cases where more than one crystal structure exists, an average density was used. There are several important general conclusions which can be arrived at from an examination of this table. Within a given group of the periodic table, the required amount of the lower molecular weight sorbents are lighter and of lower volume. For instance, the required mass and volume of sodium oxide are 8.12 kgm and 3.58 liters whereas the higher molecular weight cesium oxide requires 36.9 kgms and 8.69 liters.

Another important consideration is the valence of the sorbent cation. For instance, two univalent cations are required for each sulfate anion whereas only one divalent cation is. If these cations have approximately the same molecular weight, then the divalent one would be preferable. An excellent example is the third period of the periodic table. The first three members of this period, sodium, magnesium, and aluminum, have nearly the same atomic weight but they are, respectively, univalent, divalent, and trivalent. The required amount of sodium oxide is 8.12 kgm, of magnesium oxide is 5.28 kgm, and of aluminum oxide is 4.45 kgm. The volumes likewise decrease. Therefore, to minimize trap mass and volume, lower cation molecular weight sorbents with higher valence states are preferred.

There is another problem which must be considered in the selection of a sorbent material and in the engineering of the sorbent structure to be installed in a vehicle. This problem is the increase in volume of the sorbent as sulfur is picked up. The magnitude of this problem is shown in Table X where the volumes of the totally sulfated sorbents are given along with the ratio of the sulfated volume to the fresh sorbent volume. This volume increase is a result of two compounding factors. First, the mass of the trap is continuously increasing due to the pickup of sulfur trioxide and dioxide. Second, the crystalline density of the sulfate is always less than the corresponding oxide.

Table IX

DECOMPOSITION TEMPERATURES OF SULFATED SORBENTS

Compound	Decomposition Temperature	Determination Method	Reference
Sodium	>800°C		40
Potassium	>800°C		40
Cesium	>800°C		40
Magnesium	750°C	Thermodynamic Calculation	60
	890-972°C	In air flow	3
Calcium	1180	Thermodynamic Calculation	60
	>1200°C	In air flow	3
Barium	>800°C		40
Aluminum	652	Vacuum	58
	590-639°C	In air flow	3
	650-950°C	Inert gas flow	40
Manganese	699-790°C	In air flow	3
	880-1100°C	In air	40
Iron	630	Vacuum	58
	781-810°C	Inert gas flow	40
	702-736°C	In air flow	3
	700-840°C	In air	40

Table X

MASS AND VOLUME REQUIREMENTS OF VARIOUS SORBENTS*

Sorbent Material	Mass Req'd. (kgm)	Vol. Req'd. (lit)	Sulfated Mass (kgm)	Sulfated Vol. (lit)	Sulfated Volume, Expansion Ratio
Na_2O	8.12	3.58	18.6	6.94	1.94
K_2O	12.34	5.32	22.8	8.58	1.61
Cs_2O	36.9	8.69	47.4	11.2	1.29
MgO	5.28	1.48	15.8	5.93	4.00
CaO	7.35	2.21	17.8	6.46	2.92
BaO	20.1	3.51	30.6	6.79	1.94
Al_2O_3	4.45	1.12	14.9	5.51	4.92
MnO	9.29	1.70	19.8	6.09	3.58
Fe_2O_3	6.97	1.33	17.5	5.64	4.24
CuO	10.4	1.63	20.9	5.80	3.56
ZnO	10.7	1.90	21.1	5.97	3.14
$MgCO_3$	11.0	3.73	15.8	5.93	1.59
$CaCO_3$	13.1	4.65	17.8	6.46	1.39
$BaCO_3$	25.9	5.84	30.6	6.79	1.16
Na_2CO_3	13.9	5.48	18.6	6.94	1.27
K_2CO_3	18.1	7.46	22.8	8.58	1.15

*Assuming 131 gm. moles of sulfur to be trapped.

Unfortunately, the magnitude of this volume increase problem increases for the more desireable (from initial volume and weight considerations) sorbents. For instance, aluminum oxide has the lowest volume required, yet has the highest volume increase ratio. On the other extreme, cesium oxide has the largest volume requirement, yet the lowest expansion ratio.

One means of minimizing this problem is to provide for this expansion chemically by using a sorbent which gives up some mass as it picks up the sulfur oxides. This exchange reaction must release a compound which itself is not a deleterious emission. One class of ideal exchange sorbents are the metal carbonates which release carbon dioxide in exchange for sulfur oxide . Several potential carbonates are listed in Table X. where their volume and mass requirements are shown. It is immediately obvious that the volume and mass of the carbonate sorbents is much greater than for the oxide, however, the volume expansion is drastically reduced. Use of the carbonates would simplify the engineering of the physical sorbent structure by eliminating the need for large volume expansions. This simplification more than outweighs the initial increased volume of the sorbent carbonates over the oxides.

There are two side reactions of the sorbent with exhaust gas constituents which need to be considered in selecting potential sorbent materials. The first side reaction is the reaction of the sorbent oxide with carbon dioxide to form the sorbent carbonate. This reaction is important for several reasons. If the carbonate is unreactive towards sulfur trioxide, then formation of carbonate decreases the potential sulfation capacity of the trap. If the sorbent carbonate is reactive, it is possible that the reactivity will be lower than for the sorbent oxide which would lower the reactivity of the trap. Another problem is that the formation of carbonate causes a volume expansion. This expansion within a sorbent particle causes the pore volume to decrease which, in turn, can hinder diffusion of the sulfur trioxide into the particle. Therefore, the potential amount of internal sulfation will be decreased.

The best example of carbonation is the reaction of calcium oxide. Thermodynamic calculations show (see for instance Ref. [46]) that the carbonation of calcium oxide is favorable in an exhaust gas environment at temperatures below 760°C. Thermodynamic calculations also show that the calcium carbonate formed will react with the oxides of sulfur. Thus, the possibility of carbonate formation exists and will be competitive with the sulfation. If the carbonate is formed, it can also react with the sulfur oxides. However, the possibility exists that this reaction will be significantly slower than the reaction with the oxide which would lower the overall activity of the trap. There are no rate data available which are applicable to exhaust gas concentrations and temperatures. Therefore, the possible activity reduction cannot be determined or estimated.

Table XI

SOLUBILITIES OF VARIOUS FRESH AND SULFATED SORBENTS
SOLUBILITIES IN GRAMS PER 100 ML. OF COLD WATER

Sorbent Material	Oxide Solubility	Carbonate Solubility	Sulfate Solubility
Sodium	d.*	7.1	S.
Potassium	v.s.	112	12
Cesium	v.s.	260.5	167
Magnesium	0.00062	0.0106	26
Calcium	0.131	0.0015	0.209
Barium	3.48	0.002	0.0002
Aluminum	i	----	31.3
Manganese	i	----	52
Iron	i	0.0067	sl. s.
Copper	i	i	14.3
Zinc	0.00016	0.001	S

* d. - dissolves
v.s. - very soluble
S. - soluble
sl.s - slightly soluble
i - insoluble

The amount of pore volume reduction due to volume increase upon carbonation can be estimated from Table X. For the same equivalent of calcium, the carbonate requires 2.10 times the volume of the oxide. Therefore, if the initial particle of calcium oxide had a porosity of 50%, complete carbonation would fill all of the pore volume assuming all expansion is internal and no reaction occurs with sulfur oxides.

These same problems are also present with essentially all potential sorbent oxides. Since the desired type of sorbent reaction, a basic sorbent with the acidic sulfur oxides, is the same as for carbonation, potential sulfur oxide sorbents will also react with carbon dioxide.

The second detrimental side reaction is that of either the fresh or sulfated sorbent with water. The main problem associated with the reaction of water is the volume expansion of the bed at low temperatures such as during startup. Several of the sorbent oxides can react with water to form hydroxides and most of the sulfated sorbents are highly hydroscopic and form hydrates with as many as 18 molecules of water per molecule of sulfated sorbent (i.e., $Al_2(SO_4)_3 \cdot 18\ H_2O$). These added water molecules cause a volume increase which can plug pores and even increase pressure drop across the catalyst bed. Since the water of hydration is driven off even at very low temperatures, the problem of volume increase would be applicable only at startup.

Both possible side reactions apply to almost all potential sorbents. The degree to which these reactions would decrease the activity and/or capacity of a sulfate sorbent is a very complex question which cannot be answered without direct experimentation under exhaust gas conditions. Since all potential sorbents could exhibit these problems to some unknown degree, a selection of potential sorbents using the criterion of deleterious side reactions is impossible.

Since the sulfate trap must operate in an environment where contact with liquid water is highly probable at many times during the lifetime of the trap, the fresh and sulfated sorbent should be insoluble. Dissolution of the fresh sorbent would decrease the total sulfation capacity of the trap. Dissolution of either or both the fresh and sulfated sorbent would decrease the structural strength of the sorbent particles possibly leading to increased attrition and/or channelling.

The solubilities of several potential sorbent oxides, carbonates and sulfates are given in Table VI. These values were all obtained from reference [10]. The table shows that the oxides, carbonates, and sulfates of the alkali metals are all quite soluble with the solubility increasing with increasing molecular weight. The alkaline earth oxides show more favorable solubilities. Magnesium and calcium oxides have acceptable solubilities. Barium oxide is more soluble and could present

some problems. The carbonates of the alkaline earth series all have acceptable solubilities. The solubilities of the sulfates decreases with increasing molecular weight. The solubility for magnesium sulfate would be borderline while the higher molecular weight members would be acceptable.

The oxides and carbonates of the transition metals are insoluble or, at worst, only slightly soluble. The sulfates are, however, quite soluble with the exception of iron which is only slightly soluble.

Based on solubility restrictions, none of the alkali metals would be acceptable. Calcium of the alkaline earth metals would be acceptable, and iron of the transition metals listed would be acceptable.

Another consideration of somewhat lesser importance in selecting potential sorbents is the cost and availability of materials. The real importance of cost and availability would come if two sorbents were to show equal potential. However, for screening purposes, only those materials which are in short supply or are very costly should be eliminated.

For reference, the costs of several potential sorbent materials are listed in Table VII. The cost listed is for enough material to trap 131 gm. moles. of sulfur. All material costs were obtained from Reference [9] and pertain to bulk quantities f.o.b. New York. The first cost column assumes that the trap material can be prepared by some simple, mechanical treatment, e.g. pelletization. The costs for the transition metals are based on the bulk metal rather than the oxides. The second cost column was developed assuming that a soluble salt, in this case the nitrate, would be required as the raw material in a precipitation procedure.

The first cost column shows that the least expensive sorbents would be the oxides of the alkaline earth metals followed by the transition metals. In all cases, the cost of the soluble nitrate salts were higher than for the oxides. Also, the cost of preparing the sorbent from the salt would be greater than from the oxide.

Ideally, the construction of the trap would preclude fresh or sulfated sorbent attrition. However, in practice attrition and emission of the trap material will occur. Therefore, emissions of the fresh and/or sulfated sorbent cannot be harmful. Two examples immediately stand out: beryllium and lead. Beryllium, the lowest molecular weight alkaline earth metal, would be an ideal sorbent cation from many of the considerations discussed above. However, beryllium oxide and sulfate are extremely toxic [57] and, therefore, must be eliminated from consideration. The same is true for lead. The lead oxide candle procedure for quantitative sulfur dioxide measurement shows an excellent sorptive activity but lead oxide and sulfate emissions are harmful. Hence, lead must also be eliminated as a potential sorbent.

Table XII

ESTIMATED COSTS OF VARIOUS SORBENTS

Sorbent	Molecular Weight	Kgm of Sorbent per trap	Estimated Sorbent Cost	Sorbent Cost Nitrate Salt
MgO	40	5.2	0.50	14.00
CaO	56	7.3	0.20*	---
BaO	153	20.0	6.80	11.00
Ni	59	7.7	27.00	23.00
Cu	64	8.4	10.00	23.00
Zn	65	8.5	6.50	7.70
Mn	55	7.2	5.20	---

* from limestone

In selecting potential sorbents based upon these considerations, there is no single material which stands out in all categories. The one cation which is consistently near the top in all categories is calcium. This cation could be employed either as the oxide or as the carbonate. Other potential sorbents which show promise are magnesium, manganese, and aluminum. Again, the most probable sorbent would be the oxide of these materials. The remaining potential sorbents have deficiencies in one or more categories.

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